

## **Xenobiotic Organic Compound Cycling In Coastal Waters**

Philip M. Gschwend

Ralph M. Parsons Laboratory, 48-415  
Massachusetts Institute of Technology  
Cambridge, MA 02139

phone: (617) 253-1638 fax: (617) 253-7395 email: [pmgschwe@mit.edu](mailto:pmgschwe@mit.edu)

Ken O. Buesseler

Clark 447, MS#25

Woods Hole Oceanographic Institution  
Woods Hole, MA 02543  
508-457-2309

phone: (508) 457-2309 fax: (508) 457-2193 email: [kbuesseler@whoi.edu](mailto:kbuesseler@whoi.edu)

Award # N00014-93-1-0883

[http://www.onr.navy.mil/sci\\_tech/ocean/onrpgahj.htm](http://www.onr.navy.mil/sci_tech/ocean/onrpgahj.htm)

### **LONG-TERM GOAL**

Our long-term goal is to develop the basis for predicting the fates of xenobiotic organic chemicals in harbors and coastal marine environments. To this end, we seek to build a flexible modeling approach that is capable of yielding estimates of chemical concentrations in space and time, and which is tunable for various compounds and coastal environments of interest. Such predictions are necessary to allow us to manage wisely our coastal discharges and to evaluate the need to clean up existing conditions.

### **OBJECTIVES**

In order to assess xenobiotic organic chemicals which are hydrophobic (HOCs) in coastal marine environments, we must be able to (1) characterize each chemical's speciation, and (2) evaluate the rates of processes affecting particles in coastal seawater. The first objective requires us to examine the distribution of contaminants like PCBs and PAHs among dissolved, colloidal, and settling-particle phases. Moreover, we seek to find properties of the sorbates, sorbents, and solutions from which these "phase" distributions can be estimated *a priori*. The second objective requires us to assess quantitatively the fluxes of solids from the water column to the sediment beds below.

### **APPROACH**

In the last year, we have pursued two approaches for examining the cycling of organic contaminants in coastal seawaters. First, we used fluorescence observations of the probe fluorophore, methyl perylene, to observe the importance of partitioning of such hydrophobic organic chemicals to the air-seawater interface. Secondly, we sought to assess the effectiveness

## Report Documentation Page

*Form Approved*  
OMB No. 0704-0188

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE <b>1998</b>	2. REPORT TYPE	3. DATES COVERED <b>00-00-1998 to 00-00-1998</b>		
4. TITLE AND SUBTITLE <b>Xenobiotic Organic Compound Cycling In Coastal Waters</b>			5a. CONTRACT NUMBER	
			5b. GRANT NUMBER	
			5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)			5d. PROJECT NUMBER	
			5e. TASK NUMBER	
			5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Woods Hole Oceanographic Institution, Woods Hole, MA, 02543</b>			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)	
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release; distribution unlimited</b>				
13. SUPPLEMENTARY NOTES <b>See also ADM002252.</b>				
14. ABSTRACT				
15. SUBJECT TERMS				
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT <b>Same as Report (SAR)</b>	
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>		
			18. NUMBER OF PAGES <b>4</b>	19a. NAME OF RESPONSIBLE PERSON

of our chemical fate modeling by contrasting our predictions of the concentrations of linear alkyl benzenes, a group of hydrophobic organic compounds with a well-defined source to coastal water, with measurements we have made of their occurrence in coastal seawater and sediments. In this effort, we applied our U238-Th234 derived sedimentation rate coefficients, along with particulate concentrations of the organic compounds, to calculate the export fluxes of those organic chemicals from the water column.

## WORK COMPLETED

We used the fluorescent probe, 1-methylperylene, to measure the affinity of hydrophobic (as opposed to amphiphilic) compounds for the air-water interface (Gustafsson and Gschwend, in press). We completed this investigation by demonstrating that our findings fit an extrapolation of literature data available for much less hydrophobic substances.

We also used linear alkyl benzenes (LABs) as molecular markers of coastal pollution in large urban harbors to examine our ability to predict the fate of HOCs released in urban harbors to and within adjoining offshore waters. The approach was applied to Boston Harbor and the adjoining waters of Massachusetts Bay and Cape Cod Bay. Estimates were made of both the phase speciation and the rates of the different processes affecting each HOC's fate. These parameters were used to make predictions of LAB concentrations, and these predictions were compared to our field measurements.

## RESULTS

We found the water-air/water interface partition coefficient for the polycyclic aromatic hydrocarbon, methylperylene, to be:  $K_{w\text{-awi}} = 1.2 \text{ mol/cm}^2 \text{ awi}/(\text{mol/mL}_w)$ . This result is consistent with an extrapolation of partition coefficients reported in the literature for much less hydrophobic PAHs, distributing themselves between the same interface and air. In fact, our combined results lead to a predictive equation for water/air-water interface partition coefficients of aromatic hydrocarbons:

$$K_{w\text{-awi}} = 10^{-10.4} (P_L)^{-0.20} \gamma_w$$

where  $K_{w\text{-awi}}$  is the partition coefficient in (mol per  $\text{cm}^2$  of interface/ mol per mL of solution),  $P_L$  is the (hypothetical) liquid vapor pressure in atmospheres, and  $\gamma_w$  is the aqueous activity coefficient in reciprocal mole fraction.

Our results demonstrate significant partitioning from bulk water to the water/air interface for a hydrophobicity range relevant to many xenobiotic compounds (e.g., 5-ring PAHs, highly chlorinated PCBs).

The mass balance box modeling of LABs in Boston Harbor and the adjoining waters of Massachusetts Bay and Cape Cod Bays suggested that fates of LABs are controlled to similar extents by (1) horizontal flushing, (2) vertical scavenging, and (3) microbial degradation. In contrast, the sinks due to indirect photolysis and volatilization were initially suggested to be minimal. By comparing these modeling predictions with our field measurements of LABs in

seawater, we found that we could not match those observations without adding an additional sink to the modeling calculations. Moreover, that sink must preferentially eliminate "internally substituted" LABs over their "externally substituted" isomers. In light of these discrepancies and our observations of the substantial partitioning of hydrophobic compounds to the air-water interface (Gustafsson and Gschwend, *in press*), we speculate that the "missing sink" may involve (1) partitioning of LABs to the air-water interface and then either (2a) enhanced mass transfer to the atmosphere or (2b) enhanced transformations due to interactions with atmospheric oxidants.

## **IMPACT**

We anticipate that the very substantial partitioning of hydrophobic compounds (note: these compounds must not be confused with amphiphiles) from aqueous solution to the air-water interface may have important ramifications for the intensities of numerous environmental processes affecting fates of those compounds. For example, water-to-air transfers could be greatly enhanced over current model predictions which identify the water-side diffusive boundary layer as the critical bottleneck for export of PAHs to the atmosphere. Likewise, transformations of such substances in coastal seawater environments may include, not only solution phase processes, but also reactions with tropospheric species (e.g., hydroxyl radical) since these low-solubility organic pollutants may occur at important concentrations adjacent to marine air.

## **TRANSITIONS**

Our work will influence efforts to establish the capacities of harbors and coastal environments to act as receiving waters for hydrophobic organic pollutants (such criteria are needed by the Navy to evaluate their discharge practices at their harbor facilities.) Our findings will also assist colleagues trying to promote the biodegradation of hydrophobic pollutants, a process that is undoubtedly controlled by those chemicals' bioavailabilities.

## **RELATED PROJECTS**

All of the Navy-supported projects examining the biodegradability of hydrocarbons are related to our work in that the speciation of those hydrocarbons plays a central role in controlling microbial access to those prospective hydrocarbon substrates.

## **REFERENCES**

Gustafsson, Ö. and P.M. Gschwend. Hydrophobic Organic Compound Partitioning from Bulk Water to the Water/Air Interface. *Atmos. Environ.*, *in press*.

## **PUBLICATIONS**

Gustafsson, Ö., P.M. Gschwend, and K.O. Buesseler. Settling removal rates of PCBs into the Northwestern Atlantic derived from  $^{238}\text{U}$ - $^{234}\text{Th}$  disequilibria. *Environ. Sci. Technol.*, 31, 3544-3550, 1997.

Gustafsson, Ö. and P.M. Gschwend. The flux of black carbon to surface sediments on the New England continental shelf. *Geochim. Cosmochim. Acta*, 62, 465-472, 1998.

Gustafsson, Ö., K.O. Buesseler, W.R. Geyer, S.B. Moran, and P.M. Gschwend. An assessment of the relative importance of horizontal and vertical transport of particle-reactive chemicals in the coastal ocean. *Continental Shelf Research*, 18, 805-829, 1998.

Gustafsson, Ö. and P.M. Gschwend. Phase Distributions of Hydrophobic Chemicals in the Aquatic Environment: Existing Partitioning Models Are Unable to Predict the Dissolved Component in Several Common Situations. In: Bioavailability of Xenobiotics in the Environment, Chapter in a book to be published by NATO-ASI, in press.

Gustafsson, Ö. and P.M. Gschwend. Hydrophobic organic compound partitioning from bulk water to the water/air interface. *Atmos. Environ.*, in press.